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Conoco Dolomite Hot Gas Cleanup System

Stanford Research Inst, Menlo Park, Calif

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This report analyses a proposal that EPA sponsor a large-scale pilot plant to develop the Conoco (formerly Consol) Dolomite Hot Gas Clean-up system. The report includes a history of the prior development program, the technology involved comparisons with competitive technologies in regard to technical feasibility, potential efficiency, and environmental benefits. Future funding implications are explored. The potential benefits in economy and efficiency of energy conversion are judged to be substantial, but the cost of development is high. The expected cost of the pilot plant program may be greater than funding ability. The current laboratory program should either be continued or should be terminated in a way that will insure that the knowledge already gained is retrievable.

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CONOCO DOLOMITE HOT GAS CLEANUP SYSTEM

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1 INTRODUCTION

The EPA has been supporting laboratory and theoretical development work on the Conoco (formerly Consol) dolomite Hot Gas Cleanup system. The results have been encouraging, and Conoco Coal Development Company has proposed expanding the program to include development on a pilot plant scale at Rapid City, South Dakota, adjacent to an ERDA-sponsored gasifier pilot plant. This would entail a substantial increase in funding at a time when EPA's budget is being reduced. To help decide on the level of funding and priorities appropriate to hot gas cleanup, EPA contracted with Stanford Research Institute (SRI) to review the program and prepare briefing reports. A preliminary briefing was given in Washington, D.C., on October 21, 1975. The present document is the final briefing report of this project. The main purpose of this report is to evaluate the Conoco pilot plant proposal.

SRI reviewed available reports and other information on the Conoco dolomite system and its competitors and made appropriate plant visits and direct contacts with personnel involved in development programs. This report includes:

- A history of the program,
- The technology involved,
- Comparisons with competitive technologies in regard to technical feasibility, potential efficiency, and environmental benefits,
- Future funding implications.

II SUMMARY AND CONCLUSIONS

The main conclusions of this report are:

- The Conoco proposal, estimated to cost more than $18 million, would probably lead to substantial overruns of cost and time.
- The Conoco process would be applicable to advanced gasification/combined-cycle (GCC) power systems, expected to be developed. However, it is not applicable to any commercialized gasification process.
- The Conoco process would reduce coal consumption (estimates range from 5% to 15%) and hence reduce environmental effects of coal mining. However, it would lead to greater emissions of SO_2 and probably NO_x than conventional cold gas cleanup.
- The economic potential of the process is shown by the following estimates of power costs:
  - BCR gasifier--Conoco process--16.7 mills per kWh
  - BCR gasifier--Selexol process--21.2 mills per kWh
  - Conventional coal-fired steam plant--19.8 mills per kWh.
- The Conoco process would be operated at higher gas temperature than competing hot gas cleanup systems under development. Accordingly, the Conoco process would be more efficient.

SRI concludes that there is little chance of meeting the projected time and cost schedule with the Conoco process in its present state of development. This conclusion is based on a comparison of the requirements of the proposed pilot plant program with those of the analogous program to develop the CO_2 Acceptor Coal Gasification process. The proposed program includes four separate process developments--gasification, desulfurization, particulate and alkali fume removal, and liquid-phase Claus sulfur recovery--requiring six developmental reactors. The CO_2 Acceptor pilot plant includes only two developmental reactors. An additional basis for the conclusion is the difficulty of solving mechanical and chemical problems inherent in the Conoco hot gas cleanup process.

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However, the Conoco pilot plant proposal offers the advantages of the use of some existing facilities and a trained operating crew.

EPA support of a particular process development program depends on whether the successfully developed process would be used on a large scale. The principal application of hot gas cleanup is expected to be in GCC power systems. Technological improvements are needed for GCC systems to be more efficient and economical than conventional coal-fired steam plants with stack gas scrubbing. SRI's extensive studies of GCC systems show that they have no advantage if present commercial coal gasifiers and gas turbines are used. However, anticipated advances in both technologies will make GCC systems competitive. Other evaluations of the combined-cycle systems tend to be more optimistic than those of SRI.

This project requires development of a coal gasifier as well as the hot gas cleanup process because no suitable gasifier is already developed. Therefore, Conoco has included a development gasifier as part of its pilot plant program. This gasifier is a dry ash, fluidized-bed type which is not likely to be competitive with others under development. However, the hot gas cleanup process would be applicable to gas from other gasifiers, so the value of the Conoco program would not be negated by this factor.

The principal environmental advantage of hot gas cleanup over cold gas cleanup for GCC systems is that of reduced coal usage and a resulting decrease of environmental effects caused by mining. While potentially capable of exceeding EPA standards for new large power plants, the Conoco process nevertheless would lead to higher sulfur emissions than cold gas cleanup. The Conoco process would produce more solid wastes (spent dolomite) and probably SO_3. The comparison of particulate emissions is not clear.

All available studies indicate the Conoco dolomite process to be more economical than cold gas cleanup for GCC power plants. However, the comparisons are between a developmental process and commercial processes. Cost estimates usually rise as more is learned about the requirements of a process during development.

Competitive hot gas cleanup systems under development either operate at lower gas temperatures or are judged not to be promising. Iron oxide processes operate at much lower temperatures and therefore have less of the efficiency advantage of hot gas cleanup. Air Products and Chemicals, Inc., has recently recommended termination of its program to develop a high-temperature, fixed-bed limestone process. The technical feasibility of other hot gas cleanup systems including molten carbonate and molten metal types is regarded as doubtful.

Westinghouse proposes to remove sulfur from fuel gas in the gasifier vessel, which would restrict the use of the cleanup process to a particular gasifier. However, Westinghouse is also considering the development of a separate dolomite cleanup system, which would be a direct competitor to the Conoco system.

Experimental results of the Conoco process to date have been promising but have been more exploratory than definitive. If the decision is made to continue support, the question will remain as to the best way to proceed. The Conoco proposal might make the process available at the earliest date, but this is not certain because nonoptimal designs in large-scale equipment might require major modifications.

A more orderly program would start with construction and testing of a reliable pilot-scale gasifier, presumably funded by ERDA. Concurrently, further small-scale tests would be made on the desulfurizer-regenerator system and the liquid-phase Claus reactor. In addition, process variable studies, testing of various dolomites, and particulate removal studies would be carried out on a small scale. In these studies, reliability would be shown by closing material balances, especially those involving sulfur and alkali compound fumes.

To save time, design studies could also proceed concurrently with three objectives:

- Evaluate implications on feasibility and economics of new findings.
- Determine whether any reduction in size of the pilot plant could provide meaningful data at lower cost.
- Prepare detailed design of the proposed facilities.

This approach is common in the process industries. This period would then be followed by construction and operation of the hot gas cleanup pilot plant.

It is important to stress that should the EPA decide to abandon efforts to develop the Conoco process on a large scale at the present time, orderly termination to preserve the value of the work already done would be desirable. This would include concluding laboratory work, evaluation, and careful documentation to make the information retrievable should the program be reactivated.

III CONOCO DOLOMITE SYSTEM

Process Scheme

The Conoco dolomite system has been advanced as a method of desulfurizing hot producer gas. Particulates and alkali compounds must also be removed from the hot gas to gain the maximum potential from the system. The system may be used in combination with various gasifiers. However, the configuration analyzed here is that proposed to EPA by Conoco for a pilot plant in Rapid City, South Dakota. (The Appendix shows the configuration and material balances.)

To simplify the discussion, the process is broken down into functional blocks, as shown in Figure 1. Coal is gasified with air to make a low-Btu gas containing hydrogen sulfide (H_2S). The H_2S is removed from the gas by a circulating stream from which sulfur is removed in another system shown below. The particulates are then removed to produce a hot high-pressure clean gas. A particular point about Figure 1 is that each of the four blocks in the Conoco proposal represents a separate development project.

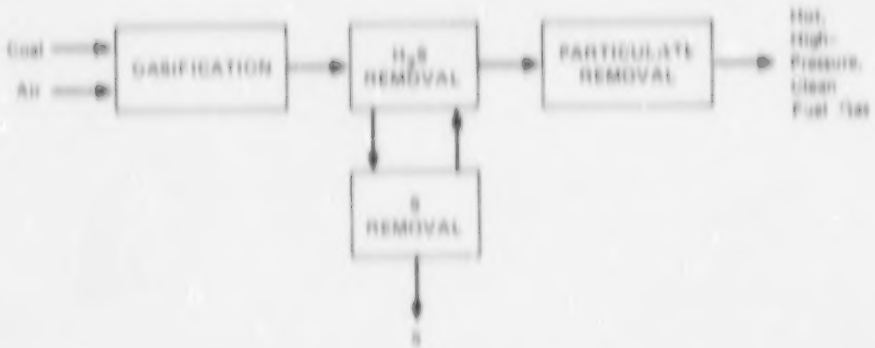

FIGURE 1 PROPOSED CONOCO PILOT PLANT

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The gasification block (Figure 2) represents three reactors: a coal pretreater, a gasifier, and a carbon burn-up cell. Gasifier development is an ERDA responsibility. It is not essential to the Conoco hot gas cleanup development except that a source of hot, dirty fuel gas is desirable for the pilot plant tests, and no suitable gasifier is available commercially.

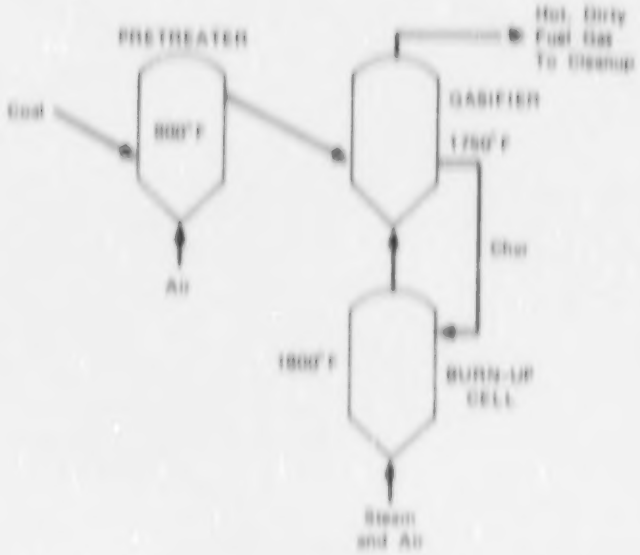

FIGURE 2 GASIFICATION OF HIGH-SULFUR COAL

Figure 3 represents the H_2S removal and particulate removal blocks. The H_2S is removed by reaction with calcium carbonate in half-calcined dolomite. Particulates and alkali compound vapors are then removed from the gas by means not yet well defined. The calcium sulfide formed by the removal of H_2S is regenerated in a separate vessel by reversal of the reaction with CO_2 and steam. The offgas from the regenerator goes to the liquid-phase Claus system shown on Figure 4 where the H_2S reacts with SO_2 to form elemental sulfur.

Conceptual Comparison with Cold Gas Cleanup

To show the potential application of this process, it may be compared with a conventional cold cleaning system for a combined-cycle power plant (Figure 5). In the cold cleaning system, the gas is cooled by exchange, wet scrubbed, desulfurized in one of many commercial processes, and reheated by exchange. The reheated gas is then burned and expanded through

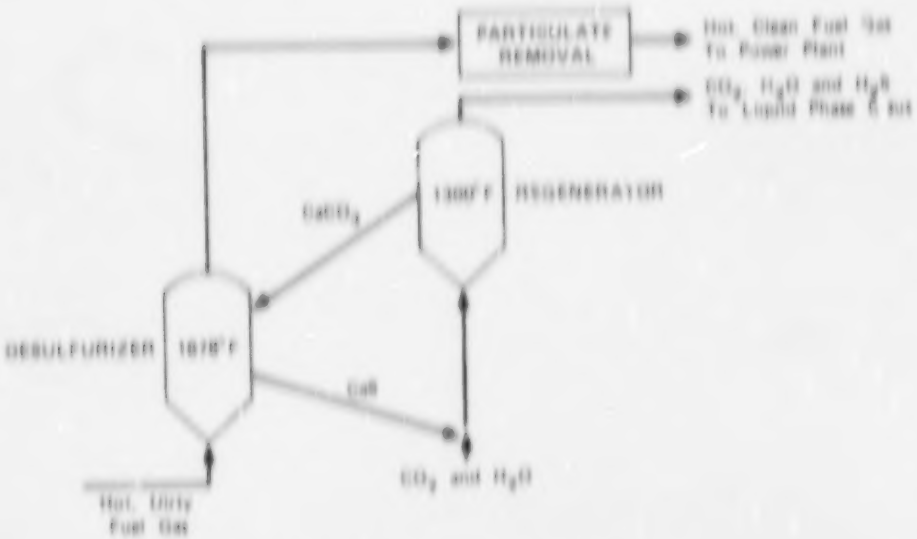

FIGURE 3 HOT GAS CLEANUP

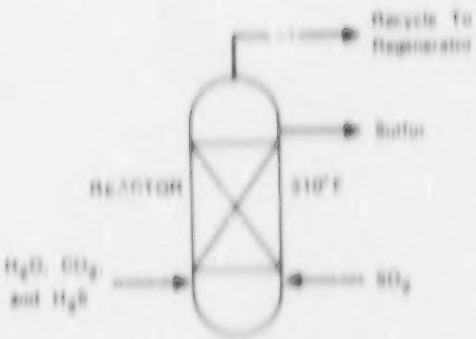

FIGURE 4 LIQUID-PHASE CLAUS SULFUR RECOVERY

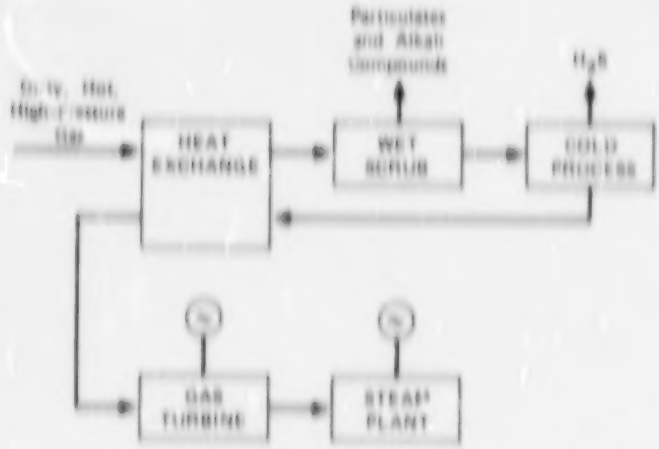

FIGURE 5 COLD CLEANING

a gas turbine. The exhausting flue gas from the gas turbine is passed through a waste heat boiler to generate steam. In hot gas cleanup (Figure 6), the heat losses and costs represented by heat exchange are eliminated. Conoco also claims an economic advantage for hot H_2S removal even if hot particulate removal proves impractical and wet scrubbing is required (Figure 7). This claim is made on the basis that cheaper exchangers can be used if they do not face the corrosive action of hot H_2S and that other process equipment is also less costly.

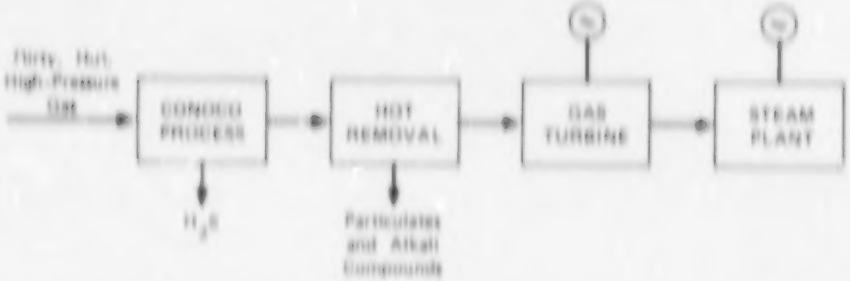

FIGURE 6 HOT SULFUR AND PARTICULATE REMOVAL

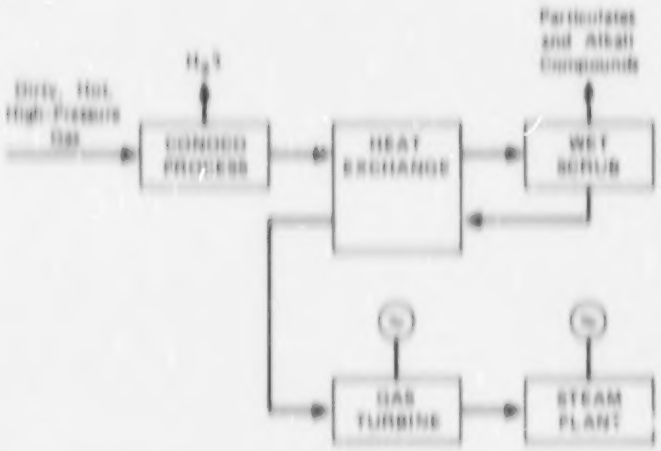

FIGURE 7 HOT SULFUR REMOVAL, COLD PARTICULATE REMOVAL

Applications, Prerequisites, and Criteria

A key consideration in supporting a development program is a judgment of whether it would be used commercially if the development were successful. Potential applications are shown below:

- Power generation, combined cycle.
- Power generation, expansion turbine and close-coupled steam plant.
- High-sulfur coals and oils.
- Intermediate pressure (~15 atm).
- Intermediate gasification temperatures (~1775°F or 968°C); desulfurization (~1650°F or 900°C).

Applications that are excluded are:

- High-Btu gas (not suitable before methanation)
- Low-sulfur coals and oils
- Methanol synthesis
- Ammonia synthesis.

Power generation with a combined-cycle system is the most attractive hot gas cleanup application. Another application would be power generation in a plant with an expansion turbine and a close-coupled steam plant.

Potential applications would utilize intermediate pressures and intermediate temperatures because of the nature of the chemistry of the process. Conditions (proposed by Conoco) of gasification at about 15 atmospheres and 1775°F (968°C) are suitable, but considerable variations from these conditions would be feasible in particular cases. Potential process applications are shown in Table 1.

Table 1

POTENTIAL GASIFICATION PROCESS APPLICATIONS
FOR CONOCO DOLOMITE SYSTEM

Process	Pressure (atm.)	Final Gas Temperature (°F)
IGT U-Gas	21	1,500
BCR 3-stage pyrolysis	≈17	2,000
Foster-Wheeler (air-blown BIGAS)	≈30	1,700
Synthane (air-blown)*	20	1,600
Winkler (pressurized, Davy Powergas)	≈14	1,700
Texaco	27	2,000-2,500

Note: Processes operating above 1800°F may require quenching the gas before desulfurization. Pressures greater than 15 atm. will not permit the degree of desulfurization attainable by the Conoco process. Increased H_2O and CO_2 concentrations will also reduce desulfurization.

*Tested in Process Development Unit.

In addition, the Exxon fluid-bed process is probably in the right range of conditions, the Shell/Koppers-Totzek pressurized gasifier may be, and the Battelle-Union Carbide process would be if designed for higher pressure. Processes with low final gas temperatures are unlikely candidates because of tars and oils in the gas; Synthane and U-Gas may be marginal on this score.

Applications exclude high-Btu gas because the degree of removal of sulfur is not adequate before the methanation step. The process is not

applicable to low-sulfur coals and oils because these fuels are environmentally acceptable without desulfurization. It is not applicable to methanol synthesis because nitrogen and part of the sulfur are left in the synthesis gas; and it is not applicable to ammonia synthesis because the degree of sulfur removal is not adequate.

Promoters of combined-cycle systems currently disagree as to the optimum pressure in the combustors. Generally those with industrial turbine backgrounds favor lower pressures than those with aircraft engine backgrounds. SRI believes that the pressure of 15 atmospheres chosen by Conoco will be compatible with electric utility preferences in the foreseeable future.

Prerequisites for use of the process include the following:

- Process for pressure gasification of high-sulfur coal.
- Control of particulates and alkali fumes (according to application).
- Control of NO_x.

Gasification of high-sulfur coals tends to be more difficult than gasification of low-sulfur lignites or subbituminous coals, because the high-sulfur coals frequently have caking tendencies. Another prerequisite is the control of particulates and alkali compound fumes according to the application. Some applications will have more stringent requirements than others. A third prerequisite is control of nitrogen oxides. The formation of nitrogen oxides is poorly defined for the potential applications of the process, as discussed in Section V.

Potential applications of the Conoco process appear to justify its development, assuming that economical solutions are found for the technological problems. The following criteria may be applied in deciding whether a possible process is worthy of development.

- At least 90% removal of H_2S
- The hotter the better, up to gasification temperature
- Elemental sulfur product preferred
- Minimum process wastes preferred
- Economic advantage.

The potential for at least 90% removal of H_2S is desirable to allow for loss of removal capability in large-scale equipment. This

potential may be needed to meet environmental regulations equivalent to over 80% removal. The criterion that a hotter cleanup temperature is more desirable applies up to the gasification temperature. Obviously, there is no point in going above the gasification temperature, because this would require heating. Any decrease of the cleanup temperature from the gasification temperature means that part of the advantage of hot gas cleanup is lost. However, some cooling will probably be needed to remove alkali compound vapors. A process should preferably make elemental sulfur because of market and environmental considerations. Obviously, a process that produces minimum process wastes is preferred, and there is no incentive to develop a process unless it has an economic advantage.

History of the Program

Table 2 shows a summary of the history of the CO_2 Acceptor process, which is a predecessor of the proposed hot gas cleanup process. Highlights are shown starting with the initial demonstration in 1950. There was no aggressive development until future shortages of natural gas became more apparent in the late 1960s, when government support accelerated the work. The costs of the development program are of interest--$9.7 million for the pilot plant itself and $36 million for the total process development.

Table 2

HISTORY OF CO_2 ACCEPTOR PROCESS

Date	Sponsor	Subject
1950	Conoco	Laboratory demonstration
1967-4	Texas Eastern/ Equitable Gas	Laboratory program
1964-8	OCR	Bench scale work and economics
1966-72	OCR-ERDA	Design and construction of pilot plant
1972-present	OCR-ERDA	Operation of pilot plant

Cost--$9.7 million for pilot plant
$36 million total process

Table 3 shows a summary of the history of the hot gas cleanup process, as sponsored by the EPA. This was started in 1970 with the in-situ desulfurization concept of combined gasification and sulfur removal. Various adaptations of the CO_2 Acceptor process were investigated; the feasibility of producing boiler fuel was studied; and laboratory work was performed. The laboratory work included preoxidation kinetics, combined gasification and desulfurization, and acceptor cycle life. It was concluded that for a low-Btu gas in which the nitrogen from the air ends up in the product gas, there is no advantage to combined gasification and sulfur removal. In the period 1972 to 1973, the separate gasifier concept was developed and a feasibility study was performed. Laboratory work included tests of the gasifier, carbon burn-up cell, pretreatment, acceptor cycle, and liquid-phase Claus reaction. In the 1974 and 1975 period, a preliminary pilot plant proposal was developed, and laboratory work included deactivation of dolomite, makeup of dolomite to approach steady state, hardening of dolomite and attrition, reaction of calcium sulfite and hydrogen sulfide, removal of particulates and alkali fumes, and the Chance reaction.* Proposed work includes the building and operation of a pilot plant. Supporting laboratory work consists of liquid-phase Claus studies, hot fixed-bed filter and cyclone studies, trace elements analysis, a thermal gravimetric analyzer study, scanning electron microscope studies, and work on an Illinois dolomite. In addition, an environmental assessment is proposed. The cost of the program to date has been $1.2 million.

Major Studies

Table 4 lists major evaluations of the Conoco process reviewed by SRI. Conoco, Environmental Science and Engineering, United Technologies Research Center, Foster Wheeler Corp., and Stone & Webster have made or are making studies. All of these show capital cost advantages for the Conoco process compared with conventional processes, although some recognize major development problems. Besides these direct evaluations, SRI considered other major sources, such as the Aerotherm review, Gilbert Associates report, SRI combined-cycle and gasification multiclient studies, and SRI private particulate removal studies.

*$CaS + H_2CO_3 \longrightarrow CaCO_3 + H_2S$.

Table 3

HISTORY OF HOT GAS CLEANUP
EPA SPONSORED

Date	Subject
1970-71	In-situ desulfurization concept (combined gasification and sulfur removal)
	Three adaptations of CO_2 Acceptor
	Feasibility study
	Laboratory work
1972-73	Revised concept--separate gasifier
	Feasibility study
	Laboratory work
1974-75	Preliminary pilot plant proposal
	Laboratory work
Proposed	Build and operate pilot plant
	Laboratory work
	Environmental assessment
Cost	$1.2 million to date

Table 4

MAJOR EVALUATIONS OF CONOCO PROCESS

Evaluator	Competitive Processes	Conclusions
Conoco	Hot potassium carbonate	Big advantage with hot removal of particulates. Less advantage with wet scrubbing.
ESSO	Hot potassium carbonate Stretford	Conoco cheapest
UTRC/Foster Wheeler	Selexol Flue gas desulfurization	Conoco cost competitive NO_x problem
Stone & Webster for EPRI	Cold cleanup	Preliminary: economic advantage at environmental penalty

IV ADVANTAGES AND DISADVANTAGES OF HOT GAS CLEANUP

Potential Efficiency Advantages

The most promising application for hot gas cleanup processes is integrated with combined-cycle power generation (Brayton-Rankine cycle) as previously depicted in Figures 5 through 7. Combined-cycle plants are now in operation using clean gaseous or liquid fuels, in competition with steam cycle (Rankine cycle) plants burning the same fuel to raise steam. There has been only one commercial application of producer gas in a combined-cycle system (the STEAG plant in Germany). This plant uses a low-sulfur coal and does not desulfurize the gas. SRI's extensive gasification and combined-cycle studies have shown that combined-cycle systems using current gasifier and turbine technology give no economic advantage over conventional coal-fired steam power plants with flue gas desulfurization. However, expected advances in both gasifier and turbine technology will make combined cycles relatively more attractive, especially if the advantages of hot gas cleanup can be realized.

The potential efficiency advantage of hot gas cleanup (both sulfur and particulates) may not be as great as is sometimes assumed because some of the available heat can be recovered by exchange prior to cold gas cleanup. However, hot gas cleanup does offer at least 5% decrease in the coal required for a given amount of power. Thus, the capacities of the mine, gasifier, and solid waste disposal can be decreased and heat exchangers for heat recovery are not required.

If it proves necessary to wet scrub the gas to remove particulates and alkali compounds, most if not all of the potential efficiency advantage is lost. However, the hot cleanup may possibly have a lower energy requirement than the cold cleanup, depending on gas composition and process specifications.

Besides the combined-cycle approach, the hot producer gas may be expanded through a turbine without prior combustion. Such a system would be similar to power recovery from catalytic cracking unit regenerators in the petroleum industry and might be more tolerant of particulates in the gas. Hot gas cleanup would have advantages over cold gas cleanup comparable to those in combined-cycle comparisons. Unfortunately,

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the thermal efficiency of the expansion turbine approach is less, and conventional combustion with flue gas desulfurization is expected to be more economical.

Environmental Effects

Recognizing the potential efficiency and economic advantages of hot gas cleanup, we should consider environmental effects. Table 5 shows a comparison with cold gas cleanup. The main advantage is that less coal is required because of the higher efficiency, and this means less land disturbance by strip mining. The process, although meeting EPA emissions requirements, is at a disadvantage compared with cold gas cleanup in the amount of sulfur oxides emitted. Other disadvantages include more solid wastes and probably more NO_x emissions. The higher NO_x emissions result from the residual ammonia in the hot gas. The comparison of particulate emissions is not clear, because so little is known about the performance of particulate removal equipment at high temperature and pressure.

Table 5

ENVIRONMENTAL COMPARISON
WITH COLD GAS CLEANUP

Conoco Advantages

- Less coal required means less land disturbance
- Less steam required if liquid-phase Claus is successful; therefore less blowdown
- Probably less power required
- Possibly less organics in wastewater if applied to processes whose product gas contains tars and oils

Conoco Disadvantages

- More sulfur emissions
- More solid wastes with water pollution from run-off
- Probably more NO_x emissions

Not Clear

- Particulate emissions

Table 5 compares the Conoco process with a conventional coal-fired power plant with flue gas desulfurization by lime or limestone scrubbing. Hot gas cleanup produces less solid waste and probably less sulfur emissions. Comparisons of NO_x emissions, land disturbances, and particulate emissions are not well defined and would depend on specific designs.

Table 6

ENVIRONMENTAL COMPARISON WITH FLUE GAS DESULFURIZATION

Conoco Advantages

- Less solid waste
- Probably less sulfur emissions

Not Clear

- Land disturbance (depends on combined-cycle technology)
- NO_x emissions
- Particulate emissions

V TECHNICAL FEASIBILITY

Table 7 lists items to be considered in regard to technical feasibility that will be discussed in this section. The heart of the hot gas cleanup idea is desulfurization, which entails fluidized-bed absorption and fluidized-bed regeneration. Some dolomites tested have shown absorptivity and limited (but perhaps adequate) regenerability without excessive attrition in small-scale equipment. Operability of large plants may depend on maintaining adequately low attrition rates in the large equipment. The usefulness of the process depends on having adequate dolomite acceptor resources with predictable performance characteristics. The failure of the Air Products and Chemicals process (discussed in Section VI) and the great variability of dolomite properties raise some doubt on this point.

Desulfurization

Absorption is by reaction with half-calcined dolomite:

$$H_2S + MgO \cdot CaCO_3 \longrightarrow MgO \cdot CaS + H_2O + CO_2$$

Regeneration is by reversal of this reaction. Dolomite is considered preferable to limestone because removal of the CO_2 combined with MgO gives the solid a porous structure. Conoco has determined experimentally the equilibrium constant for this reaction. Equilibrium constants can also be calculated from thermodynamic data published by I. Barin and O. Knacke entitled Thermochemical Properties of Inorganic Substances (Springer-Verlag, Berlin, 1973). Constants from the latter source are about two and one-half times the Conoco values, but the Conoco values are judged to be more reliable.

Equilibrium limits the potential removal of H_2S, but more than 96% removal is possible in the Conoco scheme. Removal is increased by increasing the temperature but reduced by increasing the pressure. The temperature may be limited by deactivation of the acceptor. In the proposed pilot plant, which is integrated with a dry ash gasifier, the gasifier temperature is limited by ash fusion. Regeneration is conducted at a lower temperature than absorption. The raw exit gas from the gasifier

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Table 7

TECHNICAL FEASIBILITY

Desulfurization

- Absorption
- Regeneration
- Attrition
- Plant operability
- Acceptor resources

Particulate Removal

- Filter
- Inertial
- Electrostatic

Liquid-Phase Claus

- Reactivity
- Contaminant buildup

Gasification

- Pretreater
- Gasifier
- Carbon burn-up

Nitrogen Oxides

- Ammonia
- Atmospheric fixation
- Pressure effects

rebrats the regenerated acceptor. Therefore, the absorption temperature must be lower than the gasification temperature.

Regeneration requires reducing the temperature to make the equilibrium favorable for regeneration, although this lowers the reaction rate. There has been limited exploration of the overall effect of temperature. Raising the pressure would favor regeneration, but operation of absorption and regeneration at different pressures would raise too many problems to be recommended.

The concentration of H_2S in the regenerator gas is limited by equilibrium and perhaps by kinetics to relatively low levels, about six times that in the producer gas. The purpose of hot gas cleanup is to avoid the heat losses from cooling the producer gas to low temperatures. Unfortunately, because of its higher specific heat, the heat capacity of the regenerator gas in the Conoco scheme is roughly one-fourth that of the raw producer gas, and the regenerator gas is cooled to a low temperature in the Conoco scheme.

Attrition of some dolomites has been acceptable in small-scale tests. Conoco reports that attrition was less in the pilot plant than at the laboratory scale for the CO_2 Acceptor process. Other processes, such as the alkalized alumina and the FOSCO II, have experienced greatly increased attrition of circulating solids at larger scales. The attrition rate may depend on proper design and operation of the plant. Only large-scale tests can reliably determine the attrition rate. Therefore, the possibility of excessive attrition remains as a hazard to the success of a development program. Excessive attrition could affect the operability as well as the economics of the process; however, this possibility is not considered serious.

Conoco has found that deactivation of the acceptor through the formation of large crystallites required more make-up than did attrition. This deactivation, of course, may also be affected by plant size and design.

Particulate Removal

The collection of particulates present in hot low-Btu gases may be required for one or more of at least three reasons:

- To prevent solids from interfering with the removal of H_2S from the gas;
- To prevent emissions to the atmosphere after subsequent use of the gas as fuel;
- To protect the gas turbines in a combined-cycle power generation system.

Evidently, the fuel purpose in general poses the most severe requirements, although future environmental regulations could change this picture. Protection of the turbines requires not only that the total quantity of particulates be reduced to a very low level, but that the quantity of particulates larger than 1 to 2 microns should be reduced to a particularly low level. These measures are necessary to prevent erosion of the turbines's blades by impact of abrasive particles or buildup of solid particles on the surfaces of the turbine blades or other components.

A related problem is the presence in the gas of alkali metal compounds that have been volatilized from the coal (or oil) being gasified. These materials present a special problem because they may be present in the vapor state at the higher temperatures (perhaps 1200° to 1800°F) encountered in gasification systems. Most other inorganic compounds will be in the solid state in the same temperature range. The alkali-compound vapors are thus not collectible by the dust collection equipment that may be applicable to the particulates. However, once the temperature drops low enough (perhaps about 1200°F), the vapors can condense, characteristically forming a fine fume of solid or liquid particles in the sub-micron particle-size range. These fumes can be removed only by high-efficiency collectors. The Conoco conceptual design shows cooling to 1300°, before particulate removal.

The alkali-compound vapors might be adsorbed on solids in the system. However, the likelihood that available solids in the systems will have much affinity for adsorption of the alkali vapors is rather remote. On the other hand, once the condensation temperature of the vapor is closely approached or reached, the vapor may tend to condense on the surfaces of the nonvolatile solids. The most likely surfaces for such condensation of the alkali compounds are the particulates suspended in the gas stream. Such nucleation might deposit alkalis on larger particles that can be more readily collected. There is, perhaps, some evidence for such a phenomenon to be drawn from the distribution of alkalis in the fly ash from the burning of coal. Nevertheless, it is likely that much of the alkali material will be self-nucleated and will condense to fume particles directly. There is ample evidence for such behavior from experience with various industrial dusts that contain mechanically entrained particles of nonvolatile compounds as well as fume from the condensation of alkali metal compounds or other volatile inorganic compounds.

Conoco personnel have cited reports of experience with incineration of salty sludges in fluidized beds of sand. In these cases, volatilization of sodium was suppressed, at least in part, because the NaCl reacted with water vapor and silica to form the nonvolatile sodium silicate while releasing the chlorine as HCl. Although the reaction should indeed tend

to suppress initial volatilization of the sodium, it does not appear that the reaction would be of much assistance in collecting the sodium once it has been volatilized. NaCl can be hydrolyzed in the vapor state by water vapor, but the resulting compound, sodium oxide, is even more volatile than the NaCl.

The concern with alkalis arises not so much from the possibility of abrasion, but from the dangers of corrosion and buildup on the turbine blades. These dangers are related not merely to the amounts of alkalis but also to the quantities of other materials, particularly vanadium and sulfur, that may be present. Sulfates and vanadates of the alkali metals are known to produce specific types of corrosive attack on ferrous metals at high temperatures.

As shown by wide variations in the recommendations of manufacturers, no firm data indicate just what level of particulates or alkalis can be tolerated in gas turbines. The problem is that the gas turbines that are expected to make combined-cycle systems competitive have not yet been developed. The limits proposed by Westinghouse are the most complete and elaborately derived, but their application to turbines of the future is conjectural, and their relevance to existing turbines is not clearly established. Future turbines may use transpiration cooling, in which a cooling fluid moves away from the blades. This fluid could conceivably protect the blades from deposition. However, such considerations are outside the scope of this study.

For removal of particulates and alkalis (once the latter are condensed) from the hot gases, the general methods and devices potentially available are essentially limited to those presented in Table 8 or to closely related devices. SRI does not believe that cyclones can effectively remove the smallest particles. Cyclone efficiencies can indeed be increased by using small-diameter units and high inlet-gas velocities (the latter at the expense of increased erosion), but all available experience suggests that the ultimate practical possibilities of cyclones are distinctly limited. In any case, however, cyclones will probably be highly useful if not vital as precollectors ahead of high-efficiency final collectors.

Electrostatic precipitators are in principle well adapted to collection of fine particles at relatively high temperatures and pressures. However, their reliability is questionable under circumstances where even a relatively brief outage might permit severe damage to turbines. The upper range of temperature for precipitation is set primarily by the thermal ionization of the gas. As temperature rises, the system pressure must also be increased to suppress disruptive sparking and preserve a

Table 8

HOT, DRY SYSTEMS FOR REMOVAL OF
PARTICULATES AND ALKALI COMPOUNDS

Device	Principle of Operation	Limitations
Cyclone	Inertial deposition	Low efficiency in low-micron and submicron range
Electrostatic precipitator	Electrophoresis	Probably limited to not higher than 1600-1800°F. Reliability uncertain
Granular bed filter	Depth filter--primarily inertial deposition	Limited efficiency on fine particles if granules are large enough to permit easy cleaning
Woven metal fabric	Surface filter--primarily inertial deposition	Relatively low face velocities. Possible blinding and cleaning problems
Porous metal sheet (sintered granules or fibers)	Surface filter--primarily inertial deposition	(Same)
All types		Removal of alkali and other vapors not feasible unless temperature is reduced to produce condensation.

corona discharge. Currently, it is not known whether it is feasible to operate a precipitator above about 1600°F. The dimensional stability of the precipitator structure itself will tend to become critical at higher temperatures. If alkalis are to be collected, a maximum temperature of about 1200°F may be permissible to ensure that the alkalis are in the particulate state.

Filters provide a positive control on passage of particulates, and probably represent the best available approach. As with the other devices, 1200°F may be a practical upper temperature limit if alkalis must be efficiently collected.

The potential capabilities of different types of high-temperature filters differ substantially, but the filters can be divided broadly into two classes--surface filters and depth filters. With the surface filters, the dust collects on the face of the porous filter medium so that after an initial period the effective filter medium is the layer of collected dust itself. Such filters (comparable to conventional fabric filters) are inherently high in efficiency once the initial dust layer is formed. Filtration velocities are necessarily low if extremely high gas pressure drops are to be avoided, so that a relatively large filter area is required.

Cleaning can be effected by shutting off the gas flow and using a reversed pulse of clean gas. However, it is possible for the filter medium to become "blinded" by fine particles that may become wedged in fine pores of the filter medium and thereafter not be dislodged by the normal flow of clean gas.

With the depth filters (typically composed of deep beds of granules or fibers), the interstices in the packing are large and particles filtered from the gas are intercepted by the packings and deposited within the porous structure. Reducing the size of the packings and increasing the depth of the bed both increase the efficiency of particle collection, but at the cost of increased gas pressure drop, which in turn may require use of lower gas velocities and greater filter face areas for a given gas flow.

The necessity for cleaning the filter at frequent intervals or continuously imposes restrictions on the form and size of the packings. Cleaning essentially involves taking the bed apart, removing the collected dust present in the interstices or adhering to the packings, and then reforming the bed. Such a procedure is not practical with fibrous packings, but can be carried out with granular packings. Also, the granular packings must be relatively coarse (probably not smaller than 2 to 3 millimeters in diameter), since they must be cleanly and easily separated from the collected dust. The bed must be reformed simply by allowing the granules to flow back into place.

Both intermittent and continuous cleaning systems have been used with granular-bed filters. In the first system, the bed is periodically fluidized by a reverse jet of clean gas, which carries off the collected dust to a secondary collection system. In the continuous cleaning systems, the granules are fed into the filter and then withdrawn as they become loaded with collected dust. The dust is then dislodged and separated by running the granules over a screen, or by some equivalent procedure.

Because of the relatively large permissible size of the granules, the collection efficiency for fine dust or fume will tend to be low unless a deep bed of granules is used. A fairly high gas velocity must be used to keep the size of the filter within reasonable limits as well as to increase the filter efficiency.

In general, the basic approaches and devices for particulate collection at high temperatures and pressures are evidently available, but it appears that very little has yet been accomplished in developing the basic design data that will be necessary for selection and application of appropriate systems to gasification processes.

Liquid-Phase Claus Reaction

The liquid-phase Claus (also known as Wackenroder) reaction is:

$$2H_2S + H_2SO_3 \longrightarrow 3S + 3H_2O$$

In the proposed pilot plant, SO_2 from a cylinder and H_2O are mixed with the regenerator gas consisting of CO_2 and H_2O vapor with H_2S at low concentration. Conditions are maintained such that little or no H_2O condenses, since condensation would put a severe thermal penalty on the process. In a commercial process based on this concept, part of the sulfur would be burned and the resulting SO_2 absorbed in water to make H_2SO_3. Such a commercial operation would be a potential source of pollution from the SO_2 content in the absorber tail gas.

The liquid-phase Claus reaction has been demonstrated in short-term tests on a small scale. The feasibility of the design may depend on the reactivity and contaminant build up in large equipment over several months. The chemistry of aqueous sulfur compound systems is extremely complex, with disproportionation, other side reactions, and corrosion being possible. The reaction rate per unit volume may be less in large equipment because of less efficient contacting of phases.

Conoco believes, and SRI concurs, that no commercial process is very suitable for the removal of H_2S from the mixture of CO_2 and H_2O that results from the regeneration of CaS. A standard Claus unit is not suitable because of the low concentration of H_2S and the high concentration of H_2O. The high partial pressure CO_2 would adversely affect other processes, such as Stretford. Unfortunately, this means that another process development is required for success of the desulfurization process. However,

the gas out of the liquid-phase Claus reactor is not emitted to the atmosphere, so the removal requirement for H_2S is lenient, although residual H_2S will repress the regeneration of the acceptor.

From the standpoint of the desulfurization and liquid-phase Claus systems, the pressure of gasification should be as high as feasible for meeting sulfur removal requirements. High pressure promotes regeneration and gives increased concentrations of H_2S in the regenerator offgas.

Gasification

The primary purpose of hot gas cleanup is sulfur removal; therefore, it is applicable only to fuels with sulfur contents too high to meet emissions standards. Conoco proposes to use Illinois No. 6 coal in the development program. A dry ash, fluidized-bed gasifier is proposed. Illinois No. 6 is a moderately caking coal, and successful operation of this type of gasifier requires that the caking tendencies be destroyed by low temperature oxidative pretreatment. Both the gas and the pretreated coal are transferred to the gasifier. This type of gasifier does not consume all the carbon; therefore, the solid residue is transferred to a carbon burn-up cell. The proposed system is similar to the Synthane pilot plant now under construction.

The proposed gasification system has theoretical disadvantages compared with agglomerating ash and slagging gasifiers now under development. If any of the other programs are successful, the Conoco gasifier is unlikely to find wide use. However, the hot gas cleanup system is separate from the gasifier and could be integrated with other gasifiers.

Illinois No. 6 coal is expected to be much easier to handle than strongly caking coals like Pittsburgh seam. If the proposed Conoco program is successful, a proposal to extend the work to more difficult coals is likely.

Nitrogen Oxides

Finally, feasibility depends on meeting nitrogen oxides requirements. The Conoco process will not remove ammonia, which is a capability and necessity of cold aqueous cleanup systems. Ammonia may lead to more NO_x, depending on the conditions of combustion. NO_x formation from the combustion of ammonia-containing fuel gas does not correlate well with the equilibrium of the nitrogen-oxygen system.

Increased nitrogen oxides formation is not necessarily an unavoidable consequence of hot gas cleanup. Some gasification systems form little ammonia from nitrogen in the fuel. Also, the nitrogen content of fuels varies widely. Most petroleum fractions have lower ratios of nitrogen to sulfur than is common in solid fuels.

In the present state of development, neither the formation of NO_x in power systems nor the environmental requirements are known. But it is possible that this factor will dictate cold gas cleanup instead of hot in some applications.

VI COMPARISONS WITH COMPETING HOT GAS CLEANUP TECHNOLOGY

Table 9 shows other hot gas cleanup processes that are competitors to the Conoco process. Only hot gas processes are considered, because many cold processes are commercially available, and for our purposes there is no reason to choose among them. There are three iron oxide processes under development: the Babcock and Wilcox, the Bureau of Mines, and the Battelle processes. None of these is far along in development. All operate at temperatures 300 to 600°F lower than the Conoco process. Regeneration forms SO_2; hence, the most likely by-product is sulfuric acid, although Foster Wheeler has a process in the development stage by which elemental sulfur can be made.

Table 9

COMPETITORS TO CONOCO PROCESS--HOT GAS CRLY

Iron Oxide Processes
- Babcock and Wilcox
- USBM (ERDA) - Sintered with Flyash
- Battelle - with Proprietary Additive

300-600°F Lower than Conoco
Make Sulfuric Acid

Fixed Bed Limestone or Dolomite
- Air Products - Abandoned

Molten Carbonates
- Battelle Northwest

Molten Metal
- IGT - Meissner - Proprietary @ 800°F

The removal of sulfur is said to be limited by equilibrium in the reaction:

$$FeO + H_2S \longrightarrow FeS + H_2O$$

However, there is considerable disagreement as to the sulfur removal attainable. Nevertheless, it is clear that reducing the temperature favors the desulfurization reaction, an effect opposite to that in the dolomite scheme, and that the equilibrium removal is independent of the pressure.

Besides the iron oxide processes, other possibilities include contacting the gas with a fixed bed of limestone or dolomite. The developer of this process, Air Products and Chemicals, has recommended termination of the project because of poor results and unfavorable economics. Although this eliminates one competitor to the Conoco process, it also raises some question as to the uniformity of results with dolomite. Unfortunately, the report on the Air Products work is not yet available.

Desulfurization by contacting with molten carbonates is being tested by Battelle Northwest. SRI believes this process does not merit consideration for combined-cycle systems until it can be proved that vaporization and entrainment of highly corrosive molten salts do not damage turbine components.

Finally, contacting with an undisclosed molten metal is said to be the basis of the IGT-Metsanor proprietary process. Because it operates at about 800°F, it has less potential for efficiency improvement than the Conoco process.

Other possibilities (Table 10) include in-situ hot gas cleanup by gasification in molten iron or molten salt, neither of which is in an advanced stage of development. Two other systems using dolomite or limestone are the EPA-sponsored Esso England CAFB oil gasification system and one version of the Westinghouse gasifier. Westinghouse is now considering desulfurization either in the gasifier or in a separate vessel. The separate vessel process would be a direct competitor to the Conoco process. The in-situ systems would not be generally applicable to gas produced by another process.

Not shown on these tables is a suggestion by Pennecott, based on thermodynamic studies, that copper is the best potential reactant for H_2S in the 1500°F range.

Table 10

OTHER POSSIBILITIES FOR IN-SITU HOT GAS CLEANUP

Gasification in Molten Iron

Applied Technology PATGAS

Gasification in Molten Salt

Atomics International
Kellogg

Dolomite or Limestone

Esso England CAFB
Westinghouse gasifier

VII ECONOMIC EVALUATIONS

Several economic evaluations of the Conoco dolomite system have been made, usually giving comparisons with established processes. All of these are based on one or another conceptual design of the Conoco system, but the estimates for competitive systems were not all derived in the same way. The results and comments on their validity are given in this section.

The most detailed work has been done by Conoco; Table II gives the results of evaluations made in 1973 assuming start-up in 1978. All of these evaluations are based on comparable conceptual designs for a constant coal rate, which is not constant power output because of varying energy requirements. The costs include only gas cleanup and sulfur recovery, not power generation. The figures are considered applicable to a power plant of about 1,400 MW capacity; based on this capacity and the higher heating value plus sensible heat above 300°F of the fuel gas, the heat rate is 8,000 Btu/kWh. In addition, an excess of 160 MW, or 11%, is generated by expansion of the fuel gas to 10 psig. The annual electrical output is assumed to be 70% of capacity.

The first column in Table II applies to the Conoco dolomite process with hot removal of particulates and alkali compounds, assuming that cyclone separators are suitable for this job. The second column is for the same desulfurization system but assumes that the gas must be cooled by exchange, wet scrubbed to remove particulates and alkali compounds, and reheated by exchange. This second cleanup method, of course, is more expensive than the first, but according to these estimates, it is cheaper than the third method shown in the third column. In the third method, the gas is cooled by exchange, wet scrubbed, desulfurized by the hot potassium carbonate process, and reheated by exchange. The advantage for hot desulfurization even with cold particulate removal depends upon relative costs of hot and cold desulfurization systems. An additional cost advantage of hot desulfurization may be cheaper heat exchanger materials resulting from lessened corrosion potential of the desulfurized hot gas.

These estimates were made by the Conoco Engineering Department. The conceptual design of the Conoco dolomite system was based on laboratory data. The conceptual design of the hot potassium carbonate

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Table 11

COSCO ECONOMIC EVALUATIONS

Basis: Nominal 1,400 MW, 70% Plant Operating Factor (6,132 hours per year)
1973 Estimate for 1978 Operation

Method of gas desulfurization	Hot	Hot	Conventional
Desulfurization process	Dolomite	Dolomite	Hot potassium carbonate
Method of particulate and alkali removal	Hot	Wet scrub	Wet scrub
Coal required			
Tons/year (6% moisture)	3,427,000	3,427,000	3,427,000
Higher heating value (Btu/year)	81.71×10^{12}	81.71×10^{12}	81.71×10^{12}
Desulfurized producer gas to station			
Flow rate (pound mols/hour)	213,701	213,214	183,957
Temperature (°F)	600	540	645
Pressure (psig)	10	10	10
Higher heating value (Btu/year)	65.19×10^{12}	64.70×10^{12}	64.57×10^{12}
HHV + sensible heat content (Btu/year)*	68.68×10^{12}	68.44×10^{12}	67.41×10^{12}
Cost analysis			
Installed plant cost ($ millions)			
1973 cost	$334.8	$343.1	$348.6
Escalation to 1978	6.5	8.1	9.3
Interest during construction	7.0	8.6	4.9
Total investment	$348.3	$359.8	$362.8
Working capital ($ millions)	$ 1.3	$ 1.6	$ 2.2

Table II (Concluded)

Annual operating costs ($ millions)			
Direct operating cost, 19[illegible] basis	$ 5.321	$ 6.500	$10,434
Acceptor at $110/ton	0.648	0.648	-
Interest on working capital at 7.5%	0.100	0.127	0.161
Capital charges at 18% investment	8.694	10.764	17.384
Sulfur credit at $8/metric ton	(2.953)	(0.957)	(0.963)
Net annual operating cost	$13.810	$17.081	$27.416
Desulfurization cost expressed			
In terms of feed coal			
Dollars per ton coal	$ 4.03	$ 4.98	$ 6.55
Cents per million Btu [illegible]	16.9¢	20.9¢	28.4¢
In terms of product gas to station			
Cents per million Btu [illegible]	21.2¢	26.4¢	34.7¢
Cents per million Btu, [illegible] + sensible heat	28.1¢	25.4¢	33.2¢
Excess power generated by expander, MW	160	118	109

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*Sensible heat content above an assumed air heater outlet temperature of 300°F.

Sources: C. P. Curran et al., "Production of Clean Pool Gas from Bituminous Coal," EPA-650/2-73-049 (December 1973)
Hot potassium carbonate evaluation reported by Consco based on its proprietary work

system was based on literature data. This estimating group had access to proprietary cost data but not to data on the selective removal of H_2S in the presence of CO_2. With this limitation, the department is considered competent to perform the cost estimate. However, a disinterested evaluator would be preferred.

Table 12 gives an updated estimate of the Conoco dolomite system with hot particulate and alkali compound removal. Comparable updates of the other systems are not available. The later estimate gives an optimistic by-product credit to sulfur.

The costs of make-up dolomite in both of these tables is based on 1% loss per cycle, with the dolomite rate 9.2% greater than the theoretical because of its inert content. In 1975, Conoco raised its estimate of make-up to 2% to account for both attrition and activity loss. This would increase the operating cost by 6.5%.

Table 13 summarizes economic evaluations of Environmental Science and Engineering, Inc. (ESE). Both the Conoco dolomite and hot carbonate estimates are based on Conoco work for a 1,400 MW facility. The ESE estimates were made by adjusting equipment sizes to a 1,000 MW scale. ESE states that the coal gasification section is not included because the costs would be identical for the two systems. This approach fails to take into account the differing efficiencies of the two desulfurization processes. The estimated annual operating cost is higher for the Conoco system than for hot carbonate because of an increase in the estimated attrition rate (said to be 5% per cycle) for which there is no sound basis. The cost given for make-up ($1,783,000 per year) does not appear to be consistent with the stated basis--that is, 5 times attrition rate and 1.4 times capacity gives $2,316,000 per year. ESE also estimated the Conoco dolomite total operating cost using a 1% make-up rate as $8.9 million per year (less than hot carbonate).

The design upon which the Stretford evaluation (third column of Table 13) is based is characterized by ESE as "speculative." Therefore, the accuracy of the estimate is unknown.

Finally, the evaluation by United Technologies Research Center (UTRC) and Foster Wheeler Energy Corporation is given in Table 14. The evaluation is based on a Selexol (a commercial process) or Conoco dolomite cleanup system downstream of a BCR two-stage entrained-flow slagging gasifier. The evaluations correctly take account of the estimated cleanup system efficiencies. However, the performances of the two systems are not the same. The Selexol design includes a water washing step to remove ammonia from the fuel gas before it enters the Selexol unit.

Table 11

CONCEPTUAL ECONOMIC EVALUATION UPDATE
REGENERATIVE ACCEPTOR DESULFURIZATION PROCESS
Base Point: July 1975, Begin Operation: January 1980
Basis: 1,500 MW, 8,000 Btu per kwh, 70% Plant Operating Factor (6,132 hours per year)

Method of gas desulfurization	Hot
Method of particulate and alkali removal	Hot
Coal required	
tons per year (6% moisture)	3,611,000
Higher heating value (Btu per year)	81.71 × 10^{12}
Desulfurized producer gas to station	
lbmole per hour	211,701
temperature	660 F
Pressure	10 psig
Higher heating value (Btu per year)	8.19 × 10^{12}
HHV + sensible heat content (Btu per year)[1]	68.68 × 10^{12}
Cost analysis (1 millions)	
Installed plant cost	
1975 cost	157.3
Escalation to 1980	11.4
Interest during construction	13.3
Total investment (1980)	171.5
Working capital	2.38
Annual operating cost ($ mill/yr)	
Direct operating cost (1980 basis)	10.170
Sorbent at $15 per ton (tentative)	0.971
Interest on working capital at 8.5%	0.201
Capital charges at 18% investment	12.651
Sulfur credit at $25 per metric ton	(4.973)
Net annual operating cost	21.419
Desulfurization cost expressed:	
In terms of feed coal	
Dollars per ton coal	$ 5.16
Cents per million Btu(HHV)	26.2
In terms of product gas to station	
Cents per million Btu (HHV)	13.3
Cents per million Btu (HHV + sensible heat)[1]	11.2
Extra power generated by expander, Kw	110

[1] Sensible heat content above 60 degrees air heater outlet temperature of 660 F.

Table 13

EB&E ECONOMIC EVALUATION[a]
Basis: 1,000 MW, Operating Factor Not Stated
Gas Desulfurization and Sulfur Recovery Costs Only
5% Attrition of Acceptor per Pass
Make-Up at $10 per Ton
(Millions of Dollars)

	Conoco Dolomite	Hot Carbonate	Stretford
Total capital investment	$31.6	$33.7	$45.7
Annual operating costs			
Total direct	$ 4.1	$ 3.1	$ 5.6
Total indirect	1.0	1.0	1.3
Costs of capital	5.3	5.7	7.6
Total annual cost	$10.4	$ 9.8	$14.5

Source: R. S. Oglesby et al., "Final Report on Engineering Analysis, Technical Feasibility, and Applicability of the Consol Process for High Temperature Gas Clean-up," EPA Contract 68-02-1330 (August 20, 1976)

Anhydrous ammonia is recovered from the wash water. Ammonia production may be economically justified, but the capital cost is somewhat higher than is necessary for desulfurization and particulate removal. If the water washing step were eliminated, NH_3 would be absorbed along with H_2S in the Selexol system and might cause deactivation of the downstream Claus plant catalyst, depending on the NH_3 concentration. Thus, the possibility of eliminating the ammonia removal step depends on the ratio of NH_3 to H_2S in the gas, which in turn depends on the N and S contents of the coal and the gasification conditions.

The Conoco dolomite estimate in Table 14 is based on a conceptual design, and the Selexol is based on cost curves developed from published data. Because UTBC plans to use higher pressures than Conoco in combined-cycle power plants, the design conditions are outside the range of the experimental data. Accuracy is estimated as plus or minus 25%. However,

Table 14

INTEGRATED SYSTEM COST SUMMARY
Basis: 8,400 Tons per Day Illinois No. 6 Coal (~1,000 MW)
70 Percent Annual Load Factor
1976 Costs

	BCR Gasifier		Conventional
	Jelsoil	Conoco	Fl.-gas Plant
Capital costs ($/kW)			
Power system cost	208	190	345
Gasification system cost	117	99	--
Cleanup system cost	89	35	81
Total plant cost	414	324	426
Owning plus operating costs (mills/kWh)			
Owning costs (17% of capital)	11.47	8.97	11.8
Operation and maintenance			
Power system	1.19	1.08	1.1
Gasification and cleanup	2.84	1.65	1.1[a]
Fuel cost at 60¢/MM Btu	5.69	4.82	5.8
Total cost of power	21.19	16.72	19.8

[a] Stack gas cleanup.

Source: United Technologies Research Center, East Hartford, Connecticut

operating cost of the gasification and cleanup systems are arbitrarily taken as 8.5% of the capital cost per year.

Table 14 also gives an estimate of a conventional coal-fired steam plant with stack gas cleanup. The cost is estimated to be higher than for the advanced gasifier--Conoco dolomite--combined-cycle system.

VIII FUNDING IMPLICATIONS

This section considers the funding implications of the Conoco-proposed development. Table 15 gives a comparison of Hot Gas Cleanup with the predecessor CO_2 Acceptor process. The number of developmental reactions is two for the CO_2 Acceptor and six, or three times as many, for the Hot Gas Cleanup process. The sizes of reactors are shown, including the pretreater, gasifier, burn-up cell, desulfurizer, regenerator, and liquid-phase Claus reactor. The proposed plant clearly exceeds the existing plant in both size and complexity. One cost factor shown favoring the proposed plant is that coal handling and preparation facilities are excluded, since they are already built, besides dolomite handling facilities, utilities, and general facilities. Also, the trained operating crew might reduce the time required for successful operation. The design, construction, and operation time for the CO_2 Acceptor plant has been nine years to date, working with noncaking feedstocks. The corresponding estimated time for the proposed Hot Gas Cleanup process is less than four years, working with caking coals. This program includes only moderately caking coals such as Illinois No. 6. If it is successful, a proposal to extend the program to strongly caking coals such as Pittsburgh seam coal is likely. The program cost to date has been $36 million for the CO_2 Acceptor, and the estimated cost for the proposed Hot Gas Cleanup process is $18 million plus a management fee to be negotiated. Based on this comparison, the extent of experimental work to date and the inflation that has been experienced, SRI believes that the time and cost estimates are optimistic.

Another qualitative method of analysing funding implications is to consider that there are actually four development processes in series. These are gasification of caking coal, desulfurization of the gas, removal of particulates and alkali compound vapors, and the liquid-phase Claus process. While not every step is essential to operation of the pilot plant, it is likely that troubles with one step will disrupt studies of another step. After nine years of work, the CO_2 Acceptor pilot plant runs are still limited to about three weeks. It is likely

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Table 15

SYNOPSIS IMPLICATIONS

	CO_2 Acceptor	Hot Gas Cleanup
Number of developmental reactors	2	6
Sizes of reactors		
Pretreater	None	10-3/4" x 6'
Gasifier	42" x 60'	48" x 60'
Burn-up cell	None	28" x 6'
Desulfurizer	None	26-3/4" x 35'
Regenerator	33" x 35'	15-1/2" x 45'
Liquid-phase Claus	None	10-3/4" x 45'
Coal and dolomite handling and preparation, utilities, and general facilities	Included	Excluded
Design, construction, and operation time	9 yr to date	4½ yr est
Program cost	136 MM to date	518 MM est + fee

that gasifier failures in the hot gas cleanup plant would disrupt desulfurization tests. Delays are costly, especially when revisions to large-scale equipment must be made.

Unfortunately, no reliable estimate of the actual cost can be made by this approach. The nature of a development project precludes accurate predictions of total costs to get a viable process.

IX FUTURE HOT GAS CLEANUP DEVELOPMENT

This section discusses the types of information on hot gas cleanup that would be desirable. Some of the information may be available from sources outside the scope of this study, so the ideas are given as suggestions rather than recommendations.

The laboratory work by Conoco has included cycling tests of dolomites but not with make-up at steady state conditions. Projections of steady state were made by mathematical analyses that appear sound. However, we suggest that a run with make-up of at least a month would be justified for a project of this magnitude. Conoco personnel made an offhand estimate that such a run might cost $200,000, which would be no more than 1% of the cost of the pilot plant program.

A steady state run of at least a month is suggested for the liquid-phase Claus process because of the complex chemistry of aqueous sulfur compound systems. Such a run would determine the build-up of contaminants, corrosion, and possible operating problems. This should be done after currently scheduled experiments on kinetics and process variables.

Because the Air Products work did not lead to a viable hot gas cleanup process with limestone or dolomite, it would be appropriate to make an engineering analysis to determine whether there are any implications to the Conoco process. The number of dolomites tested so far has been limited; further work to determine the uniformity of deposits, the suitability of other deposits, and the adequacy of suitable reserves would be in order. Some such work is already scheduled and may be adequate.

Process variables have been more thoroughly studied in the desulfurization step than in the regeneration step. More regeneration runs to determine the thermodynamic and kinetic effects of temperature, pressure, and CO_2/H_2O ratio appear desirable to aid in process optimization.

Conoco Coal Development Company is evidently not committed to any particular particulate collection system for use with its desulfurization system. However, it has carried on bench-scale studies of a system designed to collect both the particulates and alkali vapors. The basic process consists of cooling the gas to a temperature (1200 to 1300°F)

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at which essentially all the alkali vapor is expected to condense. It is hoped that most of the condensation of alkali will take place on the dust particles as nuclei. Thereafter, the relatively coarse dust particles are to be collected by cyclones or by a filter.

In tests made up through the end of August 1975, it appeared that most of the added alkali was collected in the bench-scale system. However, it had not been possible to complete material balances to account for all the alkali and demonstrate where it was actually deposited. Hence, it is not known whether the system actually worked as conceived. The experiment is a difficult one to carry out, particularly in such a small system that has a high internal surface-to-volume ratio.

The use of dust particles to nucleate condensation of the alkali vapors is probably best studied on a relatively basic level not immediately related to a gasification process. In such a basic study, the experimental conditions would have to be very closely controlled and monitored.

Bench scale work was done by Conoco at rates equivalent to about 6 to 8 pounds per hour of coal feed. The proposed pilot plant capacity is about 2,400 pounds per hour, a scale-up of about 400. Fluidized-bed reactors pose scale-up problems, and it is necessary to have fairly large pilot plants for reliable scale-up to commercial dimensions. The proposed pilot plant size is considered reasonable, although not necessarily the minimum. If the chemistry and process requirements are adequately defined, construction and operation of a facility intermediate in size between the laboratory and pilot plant scale does not appear justified. However, a fluidized-bed gasifier with a capacity of about 50 pounds per hour of coal is currently being built at Research Triangle Park. This bench-scale pilot plant could perhaps be used to obtain data to sharpen the pilot plant design. The gas production rate would be appropriate for the scale we would suggest for studying hot removal of particulates.

Table 16 summarizes some options open to the EPA in regard to the Conoco proposal. The first is to proceed as proposed by Conoco if funds are available. This would make use of a trained operating crew, which is an advantage that should not be overlooked. It would give earliest availability of the process unless such major revisions were required that they overcame the advantage of starting earlier. However, overruns are probable.

Another option is to modify the program. One of the first steps could be to build and test a gasifier, presumably under the auspices of

Table 16

OPTIONS FOR EPA

I. Proceed as Proposed by Conoco (If funds are available)
   - Use of trained operating crew
   - Earliest availability of process
   - But probable overruns

II. Modify Program
   - Build and test gasifier (ERDA)
   - Concurrent lab work:
     - Steady state desulfurization
     - Steady state liquid-phase Claus reaction
     - Testing of more dolomites
     - Particulate removal (@15 acfm)
     - Process variables
   - Concurrent design and evaluation
   - Desulfurization pilot plant

III. Carry out terminal program
   - Laboratory work to tie up "loose ends"
   - Analysis of results
   - Documentation
   - Engineering studies for guidance of possible future work

ERDA. If continuing tests of the CO_2 Acceptor process could be coordinated, this would make good use of the trained operating crew. Concurrently, laboratory work could be done. Besides the scheduled work, we would suggest steady state tests of at least a month to determine any long-term effects in desulfurization and liquid-phase Claus sulfur recovery. SRI suggests testing other dolomites to determine the suitability of other deposits and whether there is variability within a deposit.

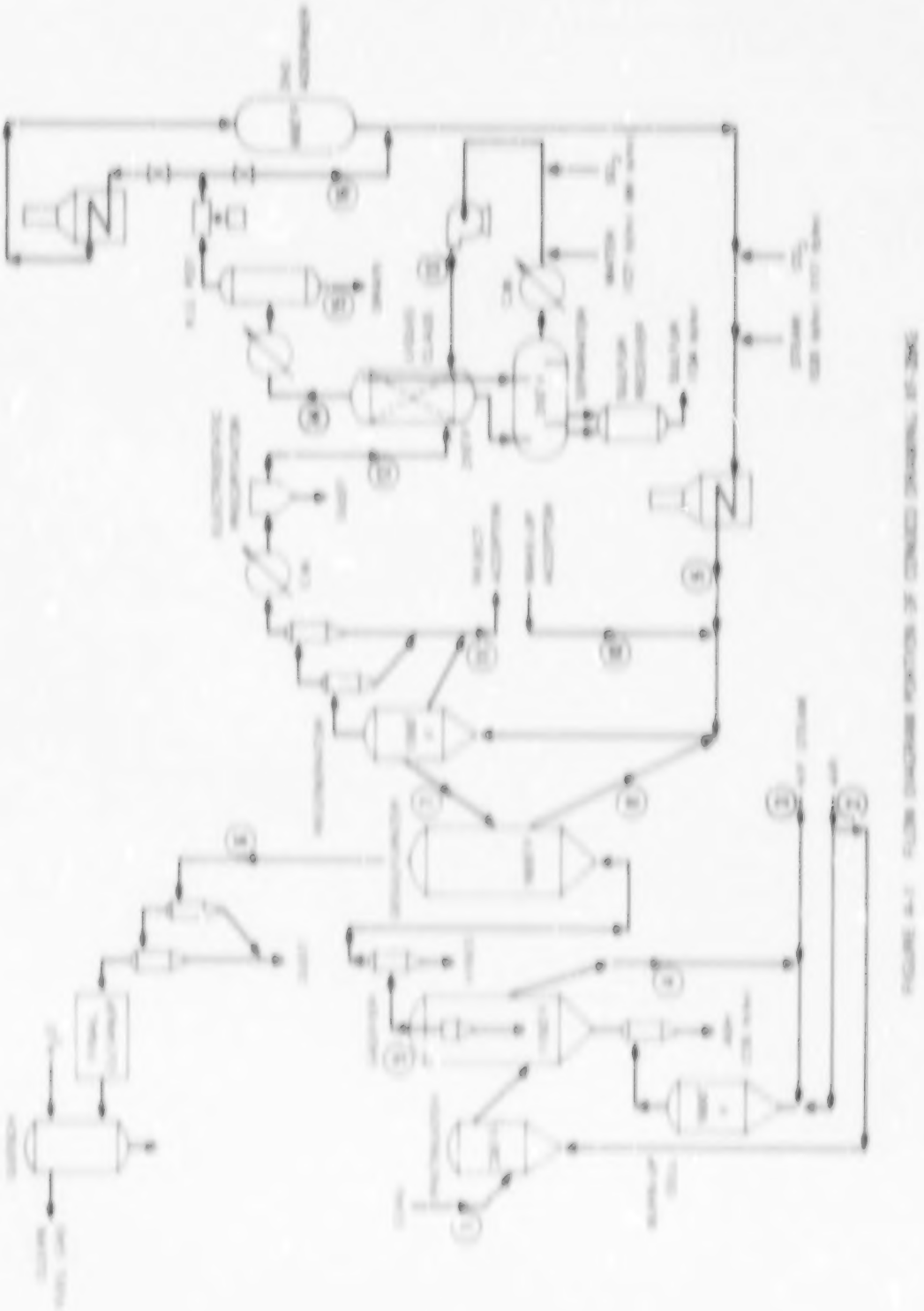
Particulate and alkali vapor removal could be studied profitably at a scale of not more than 15 actual cubic feet per minute of gas; some such work is scheduled. Process variables should be further studied to put designs on a firmer basis. To increase reliability of the data, material balances should be closed.

Design and evaluation work could profitably proceed concurrently with the laboratory work to help guide the laboratory work. This work might determine at an early date whether any new findings would invalidate the whole concept or whether any reduction in size of the pilot plant might lead to the same information at lower cost. This work might expedite the building of the pilot plant when the time comes. This approach is common in the process industries. The final step in the modified program would be construction and operation of the desulfurization pilot plant and necessary auxiliaries.

A third option is to abandon efforts intended to lead to large scale development for the present but to provide for orderly termination to preserve the value of the work already completed. This approach should entail completion of work for which the added cost would be small compared to the information gained, analysis of the results, process, evaluation and documentation in a final report. The report should give recommendations for further work in the event that the program should be reactivated.

Appendix

FLOW DIAGRAM FOR PROPOSED PILOT PLANT



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KEY STREAM IDENTIFICATION – RATES AND PROCESS CONDITIONS

Stream No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Description	Gas Feed, 80% H_2O	Air to Gasifi-cation	Steam to Gasifi-cation	Char to Burner	Gas from Gasi-fier	Gas Fuel Gas	Acceptor from Regen.	Acceptor to Regen.	Regener-ator Gas	Recovered Acceptor	Regen. Acceptor	Fuel Gas to Clean	Cleanup H_2S to Clean	Gas from Clean	Water to Steam	Gas from Clean to Power
Approx. Process Conditions																
Temperature, °F	60	1000	1000	400	1750	1600	1200	1600	1200	60	400	200	220	110	700	100
Pressure, psia	14.7	225	225	225	225	215	240	220	240	14.7	14.7	215	210	190	190	205
Hourly Flow Rates																
Pounds	2400	7594	1336	481	11,340	11,134	3279	2481	3285	45	31	3211	1082	2294	407	2402
Pound-moles		264.1	73.9		462.5	460.4			127.9			85.6	39.2	82.2	22.1	86.0
MSCF at 60°F, 1 atm		100.2	27.9		175.5	174.6			23.4			32.5		31.2		31.2
Gas Composition, Mole %																
H_2					1.6	1.6										
N_2					52.2	52.1										
CO					19.4	19.4										
CO_2					7.5	9.5			19.5			24.7		27.7	3.4	97.5
H_2O		1.1			18.8	18.5										
CH_4					0.3	0.3										
C_2H_6					0.7				1.4			2.6		4.3		0.5
C_3H_8		0.4														
C_4H_{10}													1.85			
C_5H_{12} +		0.4			0.7	0.6			0.7			2.4	98.15	40.4	99.5	2.0
Total		100.0			100.0	100.0			100.0			100.0	100.00	100.0	100.0	100.0

FIGURE A-2 MATERIAL BALANCE PORTION OF CRGCC DRAWING AT-3MC